

$[\text{Mo}(\text{dte})_4][\text{Eu}(\text{dte})_4]$ 和 $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$

的光谱电化学研究

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本文报道利用循环伏安法和紫外可见光谱法测定了过渡金属钼、镧系元素铕和铒与N,N-二乙基二硫代氨基甲酸根(dte)构成的八配位离子对配合物: $[\text{Mo}(\text{dte})_4][\text{Eu}(\text{dte})_4]$ 和 $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$ 的氧化还原特性和光谱性质。实验证实, 配合物的配正离子 $[\text{Mo}(\text{dte})_4]^+$ 比配负离子 $[\text{Eu}(\text{dte})_4]^-$ 和 $[\text{Er}(\text{dte})_4]^-$ 具备更好的稳定性和氧化还原可逆性, 同时利用现场光谱电化学法测定了配正离子氧化还原反应的电子得失个数、标准式量电位和反应速率常数。

关键词:

光谱电化学

钼铕N,N-二乙基二硫代氨基甲酸配合物

钼铒N,N-二乙基二硫代氨基甲酸配合物

电化学

STUDY ON THE SPECTROELECTROCHEMISTRY OF

 $[\text{Mo}(\text{dte})_4][\text{Eu}(\text{dte})_4]$ AND $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$

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Redox and spectroscopic properties of the eight-coordination complexes of the transition element Mo and lanthanide element Eu and Er with N,N-diethyldithiocarbamate (dte) were characterized by cyclic voltammetry and UV-Vis absorptive spectra. The complex cation $[\text{Mo}(\text{dte})_4]^+$ is more stable than the complex anions $[\text{Eu}(\text{dte})_4]^-$ and $[\text{Er}(\text{dte})_4]^-$ and possesses good redox reversibility. The electron exchange number, formal potential and rate constants of redox reactions for the complex cation were obtained by in-situ spectroelectrochemistry.

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钼 铕
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0 Introduction

The synthesis and structure related to the complexes containing molybdenum cation with dtc groups as well as lanthanide anion with dtc groups have been reported in our earlier paper^[1-2]. In the complexes, the dtc group is a two-chelate ligand which can form eight coordination and rich-sulfur complexes with pentavalent molybdenum (Mo) and trivalent europium (Eu) and erbium (Er). The two kinds of metal-sulfur bonds, i. e. Mo-S bond and lanthanide-sulfur bond, appear larger difference in respect of stability and redox properties. Since Eu and Er are light and heavy rare-earth elements respectively, the so-called "lanthanide contraction" phenomenon may bring about some influences on the properties of the complexes. The paper here will discuss their properties by electrochemical and spectroelectrochemical measurements. The study will be beneficial to understanding the bonding features of the type of complexes and applying them.

2 Experiment

1.1 Reagents

$[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$, $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ and Na(dtc) were synthesised in our lab. according to the previous reports^[1-2]. Their concentration were about 10^{-3} mol/L. In electrochemical measurement, sodium perchlorate was used as supporting electrolyte with its concentration about 0.1 mol/L. Methanol or dimethylformamide (DMF) were used as solvent, purified and dried before use.

1.2 Instrument and test conditions

Cyclic voltammetric measurement was carried out by means of a multipurpose function potentiostat (model DH-1) and a X-Y recorder (model 3086). The electrolytic cell was composed of three electrodes. Two platinum plates were used as the working and auxiliary electrodes respectively and a saturated calomel electrode (SCE) was served as the reference electrode which was connected to the cell with a salt bridge and the Luggin capillary.

UV-3100 spectrophotometer (Shimadzu, Japan) was used for measurements of UV-visible absorption spectra and thin-layer spectroelectrochemistry. Spectral data were processed by a minicomputer and plotted on a recorder of the spectrophotometer.

Spectroelectrochemical experiment was carried out by an optically transparent thin-layer electrolytic (OTTLE) cell with a platinum minigrad working electrode, a platinum plate auxiliary electrode, and a SCE reference electrode. The electrolytic cell was placed in the sample compartment of the spectrophotometer, and connected to the potentiostat. The thickness of the OTTLE cell is 0.20 mm. When the complexes were reduced and oxidized at -0.450V and -0.350V, the change of their UV-Vis absorption peaks was determined. Thus the rate constants and reaction order of their redox reactions can

be calculated. The absorption spectra after being equilibrium at different potentials for certain time were also determined in order to calculate the exchange electron number and formal standard electrode potential.

All electrochemical experiments were performed in the deoxygenated and anhydrous solutions at room temperature. During the experiment, an atmosphere of nitrogen was maintained over the solution.

2 Results and discussion

2.1 Cyclic voltammetry

Fig. 1 shows the cyclic voltammograms of $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$, $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ and $\text{Na}(\text{dtc})$ in DMF solutions containing 0.1 mol/L NaClO_4 . Their redox peak potentials are listed in Table 1. Both $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$ and $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ have a pair of redox peaks, the former peak potentials are located at -0.375V and -0.450V, the latter peak potentials are at -0.350V and -0.425V. The differences of two pair of peak potentials are 75 mV. The cyclic voltammograms of $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$ with different scan rates in DMF solution containing

0.1 mol/L NaClO_4 show that the peak potentials only have a little shift in the range of 10-400 mV/s. Experiment also shows that the current of anodic and cathodic peaks is proportional to the square root of scan rate and the peak current ratio is close to 1. According to the results above, it is a reversible electrode processes controlled by diffusion^[3], and assigned preliminarily to the following reaction: $\text{Mo}(\text{V})(\text{dtc})_4^+ + e = \text{Mo}(\text{IV})(\text{dtc})_4$. After scanning multiple cycles, the cyclic voltammograms were fixed in respect of peak potential and current. It indicates that the electroactive group is very stable.

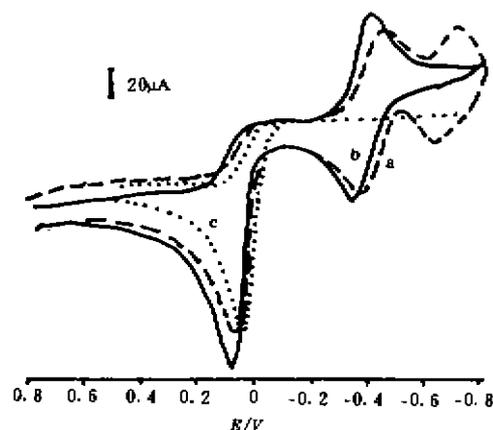


Fig. 1 Cyclic voltammograms of $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$ (a), $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ (b), and $\text{Na}(\text{dtc})$ (c) in DMF solution containing 0.1 mol/L NaClO_4 . The scan rate is 50 mV/s and the scan range is from -0.8V to 0.8V.

Table 1 Cyclic Voltammetric Data of Compounds

compounds	peak positions (vs. SCE)				
	E_{pa1}	E_{pc1}	E_{pc2}	E_{pa3}	E_{pc3}
$[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$	0.075	-0.375	-0.450	-0.640	-0.740
$[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$	0.088	-0.350	-0.425		
$\text{Na}(\text{dtc})$	0.068				

The voltammetric behaviours of $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$ are similar to those of $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ except that the former has an another pair of redox peaks at -0.740V and -0.640V while the latter has not. The voltammetric behaviours of EuCl_3 and ErCl_3 were also determined and proved that EuCl_3 has a pair of redox peaks at the same potentials as Eu-containing complex while ErCl_3 does not have any redox peaks under above conditions as Er-containing complex. It can be concluded that

the valence of Eu in its complex is changeable as follows, $\text{Eu}^{3+} + e = \text{Eu}^{2+}$.

The peak potentials of the Er-containing complex are all more positive than those of the Eu-containing complex. This may be due to so-called "lanthanide contraction". Since the ion radius of Er is less than that of Eu, the bond action to outer electrons for Er is stronger than that of Eu, so the electron loss of $\text{Er}(\text{dtc})_4^-$ is more difficult than that of $\text{Eu}(\text{dtc})_4^-$. According to the molar conductance measurement^[1], the two complexes show the weak-electrolyte feature. The complex cation and anion mainly exist in the form of ion-pair association. So the drop of ion radius of lanthanides also affects the charge distribution of $\text{Mo}(\text{dtc})_4^+$ cation. Although $\text{Mo}(\text{dtc})_4^+$ cation has the same electrochemical properties in two complexes, its redox potentials are different because of environmental difference.

It was known from Table 1 that there is an irreversible oxidation peak in the positive potential region for all three compounds in the table. The potentials of the two complexes are all more positive than that of $\text{Na}(\text{dtc})$. This may be due to the combination energy of lanthanide ions with dtc groups. Moreover the currents of the irreversible oxidation peaks are much larger than those of the former pair of peaks near -0.40V which may be because electron loss in the irreversible peak is not single. According to experimental observation, their current ratio is about 2. Thus it is possible to lose electrons on two lanthanide-sulfur bond, i. e. relating to two dtc groups.

In the two complexes, the irreversible oxidation is assigned to the electronic loss of $\text{Eu}(\text{dtc})_4^-$ or $\text{Er}(\text{dtc})_4^-$. After scanning multiple cycles the peak current decrease a little. The reason may be that the irreversible oxidation results in concentration drop of the reactant near electrode surface.

It can be concluded from the above results that in the complex compounds the Mo-S bond is stable whereas the lanthanide-sulfur bond is not too stable. According to structural analysis, the combination of central atom with dtc groups is a covalent coordination link in $\text{Mo}(\text{dtc})_4^+$ complex cation while the combination of central atoms with dtc groups is an electrostatic coordination link in $\text{Eu}(\text{dtc})_4^-$ and $\text{Er}(\text{dtc})_4^-$ complex anions^[2]. The charge of pentavalent Mo atom is higher than that of trivalent lanthanide atom, and ion radius of Mo is smaller than that of lanthanide. Thus in regard to attraction of the central atom to ligands, the former is much greater than the latter. The Mo atom holds outer electrons more firmly than the Eu and Er atoms. This means that the complex cation is more stable than the complex anion. Additionally, reduction and oxidation of the cation are gain and loss of an unbinding electron on molybdenum atom whereas oxidation of the anion is loss of bonding electrons on lanthanide-sulfur bonds. The former process does not affect the combination of Mo-S bond. This means that the complex cation is stable. But the latter process destroys lanthanide-sulfur bond. It means that the complex anion can not be recovered after oxidized.

2.2 UV-visible absorption spectra

$[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$ has similar UV-visible absorption spectra to $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ except that the former has a $f-f^*$ transition absorption at 655 nm while the latter has not. The values of peak wavelength are listed in Table 2. For the two complexes, the absorption peaks at 260 and 275 nm are assigned to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electron transition in the dtc groups. Absorption peaks at 396 and about 450 nm are assigned to charge transfer from ligand dtc to central molybdenum atom^[3]. The dtc group is an electron donor while the central Mo atom possesses much positive charge and is an elec-

iron acceptor. Therefore it easily accepts the electrons through charge transfer from dtc groups. The absorption peak at 525 nm is assigned to $d-d$ electron transition due to the pentavalent molybdenum atom under action of strong coordination field.

For Na(dtc), the absorption peaks at 257, 290 and 361 nm were observed. Similarly, the absorption peaks at 257 and 290 nm are assigned to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electron transition in dtc group. The peak wavelength difference between the two complexes and Na(dtc) may be explained by the conjugation effect of the formers.

Table 2 UV-visible Absorption Peak Position of compounds

compounds	peak positions (nm)
$[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$	259, 275(sh.), 396, 450, 525, 655($f-f^*$)
$[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$	259, 275(sh.), 396, 449, 525
Na(dtc)	257, 290, 361

2.3 Spectroelectrochemistry

By OTTLE cell, in the DMF solution containing 0.1 mol/L NaClO_4 , $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ was reduced and oxidized at a -0.450 and -0.350V (vs SCE) respectively. The change of absorption peaks in UV-visible spectra with time was shown in Figure 2a and 2b. As seen in Figure 2a, when electrolyzing at -0.450V, the absorption peaks at 396 and 449 nm decrease gradually with time. This indicates that charge transfer from dtc group to central Mo atom decreases gradually. Since

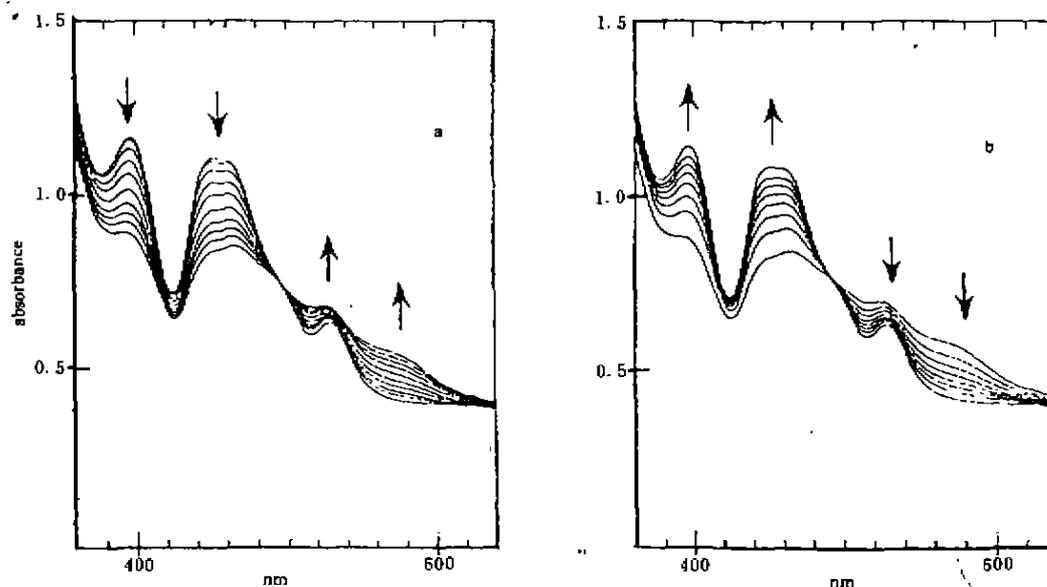


Figure 2 Change of UV-Vis absorption spectra with time for $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$ in DMF solution containing 0.1 mol/L NaClO_4 .
Electrolysis potentials: a. -0.450V(vs SCE), b. -0.350(vs SCE)

pentavalent molybdenum was reduced to tetravalent one, the charge density around Mo atom increases which results in the drop of charge transfer probability from dtc group to Mo atom. But the absorption shoulders at 525 and 580 nm increase gradually with time. This indicates that the $d-d$ electron transition probability on the Mo atom increases apparently because Mo(V) which has only one d -electron is changed gradually into Mo(IV) which has two ones.

When electrolyzing at -0.350V , as shown in Figure 2b, the change of absorption peaks with time is just opposite to the above one. It follows that the redox processes of $[\text{Mo}(\text{dtc})_4]^+$ is reversible and the change of UV-visible spectra is also reversible. Figure 2a and 2b still show that there are isoabsorptive points at 495 nm for the reduction process and at 492 nm for the oxidation process. This indicates that both reductive and oxidative states of $\text{Mo}(\text{dtc})_4$ group are stable and only the two species take part in the change.

According to the absorbance change with time, the reaction rate constants for the electrode processes, $\text{Mo}(\text{V})(\text{dtc})_4^+ + e = \text{Mo}(\text{IV})(\text{dtc})_4$, can be obtained. At first, it is assumed that the electrode processes are first-order reactions, the integral rate equation $\ln(C_t/C_0) = -kt$ may be applied, where k is rate constant, C_0 and C_t are the initial concentration and the concentration at time t for the reactant. C_0 may be expressed as $(A_0 - A_\infty)/\epsilon b$, C_t is $(A_t - A_\infty)/\epsilon b$, where A_0 and A_∞ are the absorbances of initial solution and the solution on complete reduction or oxidation respectively, A_t is the absorbance of the solution at time t , b is optical distance, and ϵ is absorption coefficient. So the above rate equation may be changed into $\ln(A_t - A_\infty) = -kt + \ln(A_0 - A_\infty)$ ^[4]. According to the absorption peak at 396 nm, the change of $\ln(A_t - A_\infty)$ with time is shown in Figure 3. Good linearity indicates that both reduction and oxidation are first-order reactions. The rate constants obtained by calculating slope are listed in Table 3. Apparently, the rate constants of the two complexes are close to each other and the reduction rate is much smaller than the oxidation rate.

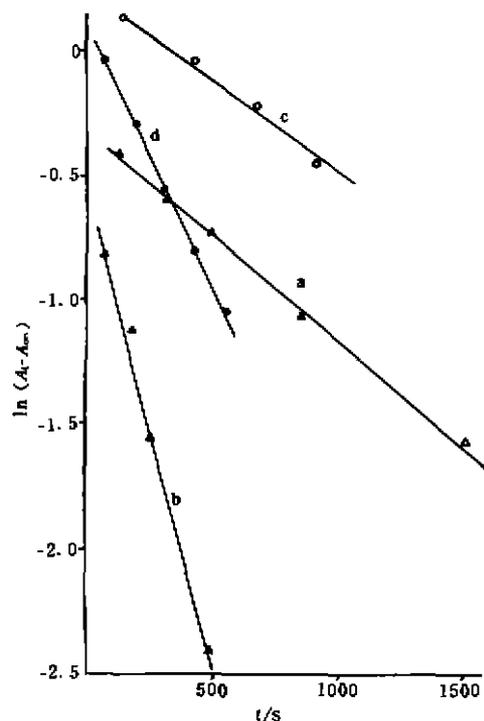


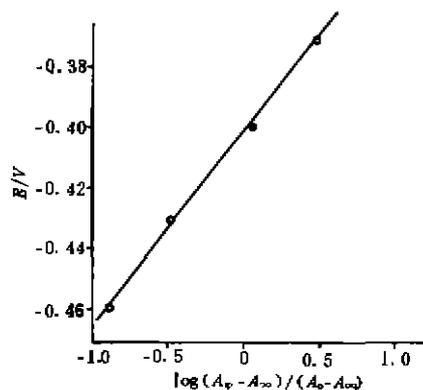
Figure 3 Plot of $\ln(A_t - A_\infty)$ with time according to the peak absorbance at 396 nm under the same conditions as Fig. 2. (a, b) $[\text{Mo}(\text{dtc})_4][\text{Eu}(\text{dtc})_4]$, (c, d) $[\text{Mo}(\text{dtc})_4][\text{Er}(\text{dtc})_4]$. (a, c) reduction, (b, d) oxidation.

Table 3 Rate constants of reduction and oxidation reactions for $[\text{Mo}(\text{dte})_4]$, $[\text{Eu}(\text{dte})_4]$ and $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$

compounds	reaction type	electrolytic	isoabsorptive	rate constant
		potentials (V)	point (nm)	$\times 10^4 \text{ s}^{-1}$
Eu	Red.	-0.500	495	7.24
	Ox.	-0.370	495	37.8
Er	Red.	-0.450	495	7.24
	Ox.	-0.350	492	21.5

The UV-visible spectra change in the range of 385-495 nm for $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$ was also determined when it was electrolyzed under different potentials in the reduction and oxidation processes. When being equilibrium at each potential, the concentration ratio of oxidative to reductive state should be fixed, and equal to $(A_{\infty} - A_0)/(A_0 - A_{\infty})$, where A_0 and A_{∞} are the absorbances of initial solution and the solution in which the electroactive species were completely reduced or oxidized, A_e is the absorbance of the solution when being equilibrium at a certain potential. Thus the Nernst equation $E = E^{\circ} + (RT/nF)\ln([\text{Ox}]/[\text{Re}])$ may

be replaced by $E = E^{\circ} + RT/nF\ln(A_e - A_{\infty}/A_0 - A_{\infty})$ ^[4], where E and E° are the electrode potential and formal standard electrode potential, $[\text{Ox}]$ and $[\text{Re}]$ represent the concentrations of oxidative and reductive states respectively. The plot of E versus $\log(A_e - A_{\infty}/A_0 - A_{\infty})$ for the reduction of $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$ is shown in Figure 4. The exchange electron number and formal standard electrode potential were obtained by calculating slope and intercept, $n = 1.10$, $E^{\circ} = -0.400\text{V}$. It proves again that the electrode processes are all single electron exchange and the formal standard electrode potential is a little negative than the average value of anodic and cathodic potentials ($E_{1/2} = -0.388$).

Fig. 4 Plot of E with $\log(A_e - A_{\infty}) / (A_0 - A_{\infty})$ for the reduction of $[\text{Mo}(\text{dte})_4][\text{Er}(\text{dte})_4]$

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